Gas Chromatography of Diisobutyrylmethane Metal Chelates

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Gas chromatographic behavior of metal chelates of diisobutyrylmethane (DIBM) was investigated. Be(II), Co(II), Ni(II), Cu(II), Al(III), Cr(III), Fe(III), Co(III) and some rare earth metals (Nd, Sm, Eu, Gd, Dy, Er and Lu) DIBM chelates were prepared. The chelates were characterized by the elementary analysis, infrared spectrum, melting point and thermogravimetric analysis. Results of the elementary analysis and infrared spectrum measurement indicated that rare earth chelates were bis-chelates unexpectedly and contained OH, although other metal chelates were normal ones. Good chromatograms were obtained for Be(II), Co(II), Ni(II), Cu(II), Al(III), Cr(III) and Fe(III) chelates, but cobalt (III) chelate was partly decomposed. Other rare earth chelates than those of Er and Lu did not give any chromatogram. This may be related to the fact that their TGA curves did not show 100% weight loss but about 75%, indicating partial decomposition.

I. INTRODUCTION

In the past several years, the volatility of metal β-diketone chelates was noticed to be an attractive characteristics and the gas chromatographic studies were carried out on the chelates of acetylacetone[1], trifluoroacetylacetone[2,3], dipivaroylmethane[4], *etc.* Especially the gas chromatographic behavior of rare earth metal chelates is very interesting from the standpoint of the rapid separation of individual rare earth elements. Sievers *et al.* reported the gas chromatography of rare earth chelates of dipivaroylmethane[4] and 1,1,1,2,2,3,3–heptafluoro–7,7–dimethyl–4,6–octanedione[5].

The authors have also taken a great interest in the gas chromatography of metal chelates and, for the systematic investigation, synthesized several β-diketones, which possessed various terminal group, and observed the volatilization characteristics and the chromatographic behaviors of their metal chelates. In this paper the diisobutyrylmethanates of various normal metals, transition metals and some rare earth metals were investigated.

II. EXPERIMENTAL

Synthesis of Diisobutyrylmethane, (DIBM), (2,6–dimethyl–3, 5–heptanedione).

A β-diketone, DIBM was synthesized by a Claisen condensation[6]. To a suspension of sodium amide in 300 ml of absolute ether, 2.0 mole of isopropylketone in 100 ml of ether and 1.0 mole of isopropylethylester in 100 ml of ether were added, and the mixture was refluxed on a steam-bath for two hours. The mixture, containing a gelatinous precipitate of the sodium salt of DIBM, was poured into water, neutralized with diluted hydrochloric acid, and then DIBM was extracted with ether. The ether was distilled out and the residue was dissolved in an equal volume of

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methanol, which was added to a hot solution containing 1 mole of copper acetate in 1000 ml of water. The copper salt of DIBM precipitated from the solution was filtered through a Buchner funnel, sucked dry on air, washed with 100 ml of ligroin and then dried. The precipitate was suspended in 200 ml of ether, to which 200 ml of 10% sulfuric acid was added, and the mixture was shaken to extract DIBM. The aqueous acid layer was again extracted with 100 ml of ether and the combined ether solution was dehydrated with sodium sulfate. The ether was distilled out and then DIBM was fractionally distilled under reduced pressure (bp, 49.0–50.0°C/4.5 mmHg). The yield was about 65%.

Preparation of Metal Chelates.

The following general procedure was designed for the preparation of the chelates of beryllium(II), aluminum(III), chromium(III), iron(III), cobalt(II), nickel (II) and copper(II). The nitrate salt of the metal (except for beryllium which was dissolved as sulfate) was dissolved in water to make a 5% solution. The metal ion solution was buffered by adding sodium acetate and mixed with an ethanol solution of DIBM. The chelate was collected by filtration, washed, recrystallized from an appropriate solvent, and dried in a vacuum desiccator over phosphorus pentoxide.

Tris-DIBM-Cobalt (III).

To a mixture of cobaltous aqueous solution and DIBM ethanol solution heated to 90°C, 10% aqueous hydrogen peroxide solution was added and the resulting solution was refluxed at 80–90°C for one hour. The precipitate thus formed was filtered, dried and recrystallized from acetone.

DIBM Chelates of Rare Earth Metal (III).

The rare earth metal chelates were prepared by the method of Hammond *et al*[7]. The metal oxide was dissolved in nitric acid. An aqueous solution of the rare earth nitrates was added to DIBM ethanol solution with constant stirring, while the pH of the reacting mixture was maintained at a value just below that, at which the metal hydroxide began to precipitate. The DIBM chelate precipitated was filtered, dried, and finally recrystallized from methanol or *n*-hexane.

Apparatus.

The gas chromatograms were obtained with a Yanagimoto GCD–5DH with a thermal conductivity detector. The column, 75 cm×3 mm i.d. stainless steel, was packed with 5% by weight of Dow Corning high vacuum silicone grease on 60–80 mesh Chromosorb W. Helium was used as a carrier gas. The infrared spectra of the chelates were obtained by the KBr disk method with a Perkin-Elmer Model 521 spectrophotometer. A Shimadzu Thermano Balance was used for the thermagravimetric measurements. About 20 mg of sample placed in a shallow platinum crucible was heated at a rate of 10°C/min. in a nitrogen stream flowing at a rate of 50 ml/min.

III. RESULTS AND DISCUSSION

All the chelates prepared were characterized by carbon-hydrogen analysis, infrared spectrum measurement and thermogravimetric analysis. Table 1 summarizes the melting point of the chelates and the results of elementary analysis. The carbon and hydrogen contents of beryllium(II), cobalt(II), nickel(II) and copper (II) chelates and of aluminum(III), chromium(III), iron(III) and cobalt(III) chelates are in good agreement with the values calculated for the *bis* DIBM chelates

Table 1. Metal chelates of diisobutyrylmethane.

Chelates	Color	mp °C	% C		% H	
			Calcd.	Found	Calcd.	Found
$Be(C_9H_{15}O_2)_2$	White	79.5	67.68	67.43	9.47	9.80
$Co(C_9H_{15}O_2)_2$	Pink	125.5	58.53	54.05	8.19	8.15
$Ni(C_9H_{15}O_2)_2$	Green	154.7	58.57	58.06	8.19	7.96
$Cu(C_9H_{15}O_2)_2$	Dark green	126.5	57.81	57.46	8.05	8.37
$Al(C_9H_{15}O_2)_3$	White	125.0	65.83	64.12	9.21	9.55
$Cr(C_9H_{15}O_2)_3$	Green	114.0	62.65	62.57	8.76	8.85
$Fe(C_9H_{15}O_2)_3$	Red	95.0	62.18	61.28	8.70	8.81
$Co(C_9H_{15}O_2)_3$	Dark green	140.0	61.82	61.46	8.65	8.70
$Lu(C_9H_{15}O_2)_2OH$	White	218.5–220.2	43.03	44.19	6.22	6.56
$Er(C_9H_{15}O_2)_2OH$	Pink	232.5–234.0	43.70	44.51	6.32	6.64
$Dy(C_9H_{15}O_2)_2OH$	White	278.0–280.5	44.13	45.13	6.38	6.52
$Gd(C_9H_{15}O_2)_2OH$	White	290.2–292.0	44.61	45.39	6.45	6.71
$Eu(C_9H_{15}O_2)_2OH$	Yellow	294.0–295.5	45.10	49.18	6.52	7.11
$Sm(C_9H_{15}O_2)_2OH$	White	294.8–295.7	45.25	48.30	6.54	7.03
$Nd(C_9H_{15}O_2)_2OH$	Lavender	294.5–295.5	45.84	49.79	6.62	7.21

and for the *tris* DIBM chelates, respectively. For rare earth chelates, however, the analytical data agree with the value for the *bis*DIBM chelates rather than that for *tris*-chelates. Infrared spectra of the rare earth chelates exhibited a sharp peak at 3620 cm^{-1} which undoubtedly arose from an OH stretching (Fig. 1.). These results indicate that the chelates formed are $Ln(DIBM)_2OH$.

Figure 2 shows a typical chromatogram, which was obtained on a multi-component mixture of DIBM chelates containing 10 μg of beryllium, 15 μg of aluminum, 25 μg of chromium, 60 μg of ferric iron and 200 μg of nickel. The figure indicates that these metals can be readily separated by the gas chromatographic technique. But aluminum, copper and cobalt (II) are not isolated from their

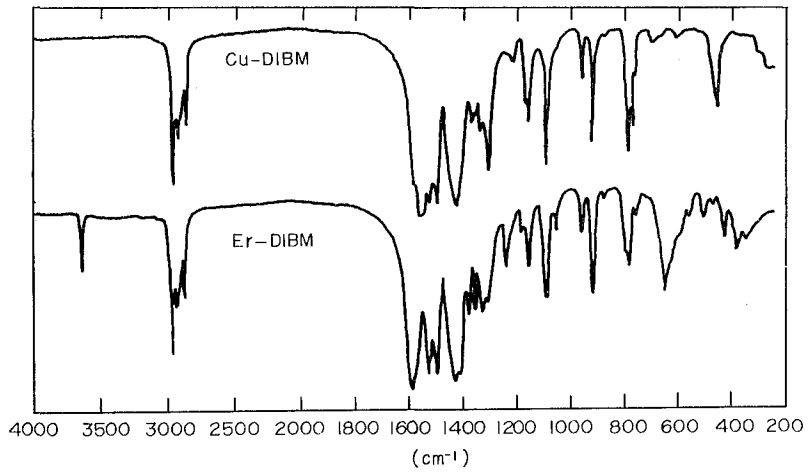

Fig. 1. IR spectra of Cu-DIBM and Er-DIBM chelates in KBr disk.

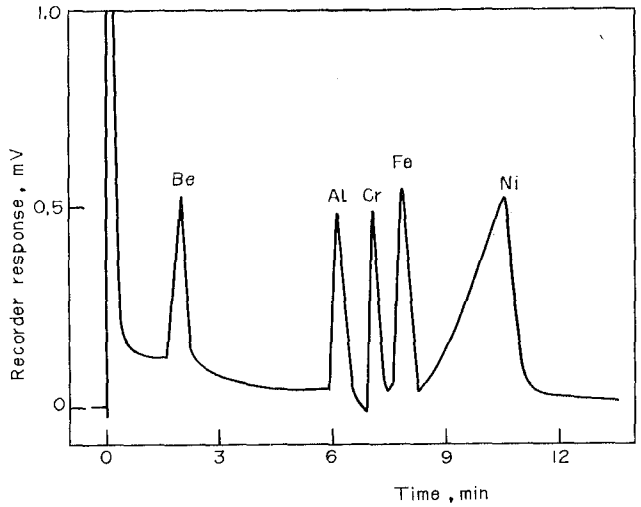

Fig. 2. The separation of $Be(DIBM)_2$, $Al(DIBM)_3$, $Cr(DIBM)_3$, $Fe(DIBM)_3$ and $Ni(DIBM)_2$.
Column temp.: programmed from 140 to 250°C at 8°C/min.
Injection port temp.: 300°C.
Helium flow rate: 45 ml/min.

mixture, because these metal chelates are eluted at almost the same time. Under the conditions described in Fig. 2, the retention times are 5.9 min. for aluminum, 6.2 min. for copper and 6.8 min. for cobalt (II).

As seen in Fig. 3, two evident peaks appear in the chromatogram of cobalt (III) chelate. One of the peaks may be attributed to Co $(DIBM)_3$ and another to

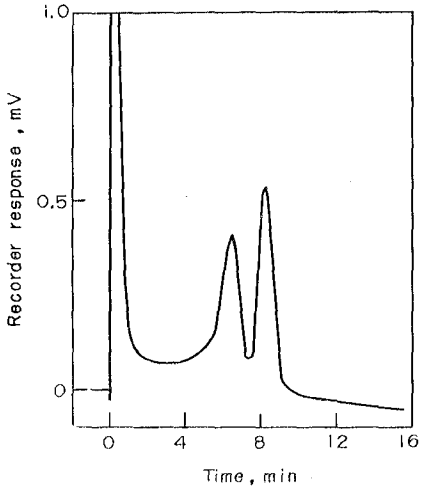

Fig. 3. Chromatogram of $Co(DIBM)_3$.
Column temp.: programmed from 150 to 230°C at 6°C/min.
Injection port temp.: 240°C.
Helium flow rate: 35 ml/min.

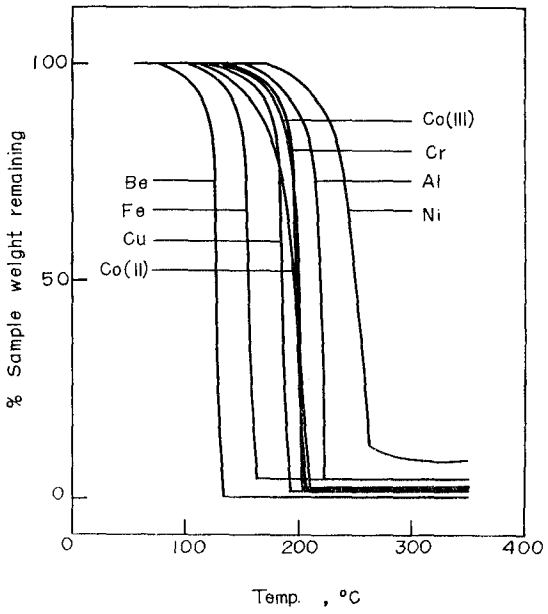

Fig. 4. Thermogravimetric curves of DIBM metal chelates.

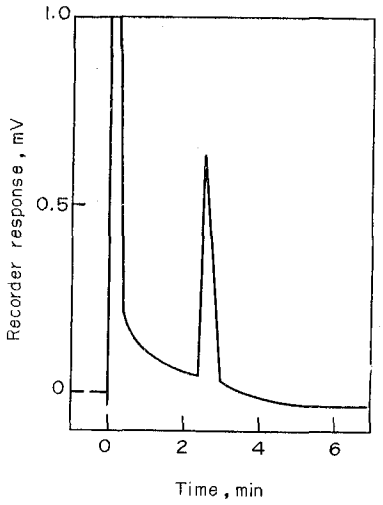

Fig. 5. Chromatogram of Lu-DIBM chelate.
Column temp.: programmed from 200 to 250°C at 8°C/min.
Injection port temp.: 270°C.
Helium flow rate: 45 ml/min.

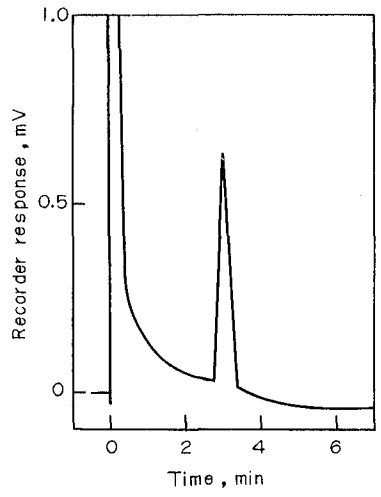

Fig. 6. Chromatogram of Er-DIBM chelate.
Conditions: same as those for Fig. 5.

the decomposed product. It could not be revealed, however, which peak resulted from the decomposition, because any attempt to collect and examine the elute was not successful. Such decomposition of cobalt (III) chelate was reported on the *tris*-acetylacetonate[2]. For this chelate only one peak, presumably arising from $Co(acac)_3$, was found. There was, however, the decomposed product in the elute.

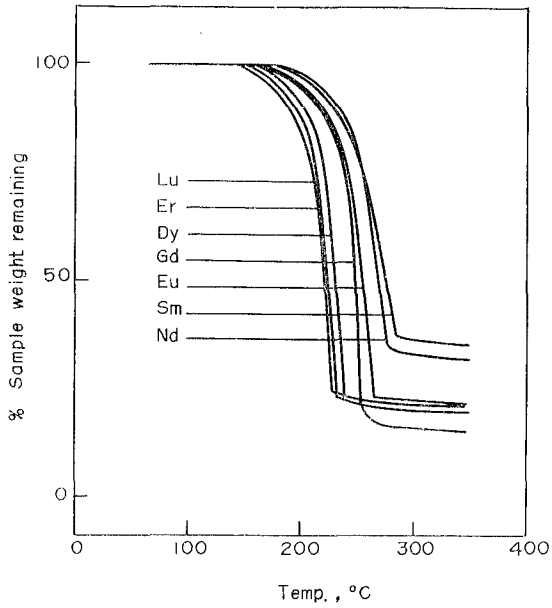

Fig. 7. Thermogravimetric curves of rare earth DIBM chelates.

Figure 4 shows the thermogravimetric curves of the DIBM chelates. The decreasing order of volatility is seen to be Be>Fe>Cu>Co(II)>Co(III)>Cr(III)>Al>Ni. This order is almost the same with that of the retention time, except that iron and aluminum replace each other.

Figures 5 and 6 present the chromatograms of lutetium chelate and erbium chelate, respectively, which were eluted at column temperature between 200 and 250°C. However, dysprosium, gadolinium, europium, samarium and neodymium chelates were not eluted at the temperature between 200 and 270°C. The sublimation-vaporisation curves of rare earth DIBM chelates in Fig. 7 indicate that their maximum weight losses are about 75% at the most. Rare earth DIBM chelates are less volatile than the dipivaroylmethane chelates, which show about 100% weight loss[4]. From such undesirable volatile characteristics and the undefined composition of rare earth chelates, DIBM is not so suitable reagent for the gas chromatography of rare earth metals, although lutetium and erbium chelates show a sharp peak in the chromatogram.

In general, DIBM chelates take place between acetylacetone chelates and dipivaroylmethane chelates in respect of the volatility, and this fact suggests that β-diketones having the sterically crowded group from the more volatile chelates.

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